

# PATENT SPECIFICATION

(11)

1 263 351

1263351

NO DRAWINGS

- (21) Application No. 31592/69 (22) Filed 23 June 1969  
 (31) Convention Application No. 156421 (32) Filed 25 June 1968 in  
 (33) France (FR)  
 (45) Complete Specification published 9 Feb. 1972  
 (51) International Classification C 23 b 5/32 5/50/5/06 5/08 5/10  
 5/14 5/18 5/26  
 (52) Index at acceptance  
 C7B 15X 1B 1E 1F 1K 1L 1P 1R 1S 1V



## (54) PROCESS FOR PREPARING THE SURFACE OF ALUMINIUM

(71) We, COMPAGNIE PECHINEY of 23 Rue Balzac, Paris 8e, France, a body corporate organised under the laws of France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for preparing the surface of aluminium or its alloys before metal-coating by electrolytic deposition.

In addition to conventional pickling operations, the electrolytic coating of aluminium or its alloys involves a special surface treatment to enable the coating applied to adhere to the surface.

The technique currently employed is zincing in an alkaline bath, for example by the process described by H. Richaud in "Corrosion et Anticorrosion", Vol. 9, No. 6, pp. 195 to 202 (1961). Unfortunately, this method is only satisfactory if the coated component does not have to undergo heating because the coatings applied have a fairly low resistance to heat and to thermal shocks. Heating to temperatures above 120°C. gives rise to the formation of blisters and also reduces the resistance to corrosion.

In another known process, the surface of the aluminium is chemically treated with an aqueous solution of zinc and nickel fluoborates. In this case, the surface of the aluminium is covered by a thin layer of zinc and nickel which enables brilliant, adherent coatings, to be subsequently obtained by electrolytic deposition, these coatings being resistant both to heat and to corrosion. However, this technique only gives satisfactory results

with non-alloyed aluminium. In cases where it is applied to aluminium alloys, the adherence of the coating is far weaker.

In our copending Application No. 37988/67 (now Serial No. 1,133,679), we disclosed an improvement comprising adding magnesium ions to the solution of zinc and nickel fluoborates. Under these conditions, outstanding results are obtained with most alloys. Unfortunately, the working conditions are fairly difficult to regulate, and it is not easy to obtain results that can readily be reproduced, above all with alloys containing copper such as copepr alloy A-U4G, for example.

The present invention relates to a process for electrochemically treating the surface of aluminium and its alloys in a bath consisting of an aqueous acid solution of zinc and nickel fluoborates. Compared with purely chemical processes, the electrochemical process according to the invention makes it possible to regulate the working conditions more easily and to obtain better results that can be effectively reproduced with alloys containing copper.

After degreasing, pickling and rinsing the components in the usual way, the process according to the invention comprises subjecting the components, which are immersed in an acid bath of zinc and nickel fluoborates and connected to the negative pole of a generator, to the action of an electric current for a period of from 5 to 300 seconds, preferably from 20 to 60 seconds.

The working conditions to be adhered to are set out in the following Table which indicates the fairly wide field in which the process may be applied and the narrower field which leads to better results.

[Price 25p]

TABLE

		Field of Application	Preferred Field						
5	Concentration of zinc fluoborate in the bath expressed in g. of zinc per litre of solution	5 to 100	10 to 30						
	Concentration of nickel fluoborate in the bath expressed in g. of nickel per litre of solution	5 to 100	10 to 30						
	pH-value of the bath	2 to 6	3.5 to 4.5						
10	Temperature of the bath (°C.)	10 to 80	20 to 35						
	Current density (A/dm <sup>2</sup> )	0.1 to 10	0.5 to 2						
	Duration of treatment (seconds)	5 to 300	20 to 60						
	<p>The baths used have a low viscosity which reduces the losses through entrainment and facilitates rinsing. They have a less aggressive effect upon the metal compared with conventional baths, thus enabling porous castings to be treated.</p> <p>Following the electrochemical treatment, the components are rinsed with water. They are then ready to be electrolytically coated with metals such as copper, nickel, chromium, tin, silver and cadmium. The coatings thus obtained are highly resistant to heating and to sudden variations in temperature.</p> <p>The following Examples are intended to illustrate the invention without in any way limiting it.</p>								
15	<p><b>EXAMPLE 1</b></p> <p>The following procedure is adopted for the chromium-plating of A-G4Z components cast in chill moulds:</p> <p>Degreasing with trichloroethylene, Alkaline degreasing in a bath containing 10 g/litre of trisodium phosphate and 10 g/litre of sodium carbonate, for a period of 2 minutes at 80°C.,</p> <p>Rinsing, Pickling in a bath of the following composition:</p> <table><tr><td>Sulphuric acid 66° Be</td><td>150 cc.</td></tr><tr><td>Water</td><td>850 cc.</td></tr><tr><td>Chromic acid</td><td>50 g.</td></tr></table> <p>for a period of 5 minutes at 55°C.,</p>			Sulphuric acid 66° Be	150 cc.	Water	850 cc.	Chromic acid	50 g.
Sulphuric acid 66° Be	150 cc.								
Water	850 cc.								
Chromic acid	50 g.								
20	<p>Rinsing, Preparing the cathode surface in the following bath:</p> <table><tr><td>Zinc (in fluoborate form)</td><td>20 g/litre</td></tr><tr><td>Nickel (in fluoborate form)</td><td>20 g/litre</td></tr><tr><td>pH value</td><td>3.8</td></tr></table>			Zinc (in fluoborate form)	20 g/litre	Nickel (in fluoborate form)	20 g/litre	pH value	3.8
Zinc (in fluoborate form)	20 g/litre								
Nickel (in fluoborate form)	20 g/litre								
pH value	3.8								
25	<p>Current density 0.5 A/dm<sup>2</sup>, i.e. a voltage across the terminals at 2.5 volts,</p> <p>Duration: 60 seconds, Temperature: 30°C., Anodes: graphite,</p>								
30	<p>Rinsing, Brilliant nickel plating in a Udylite bath at a current density of 6 A/dm<sup>2</sup> and at a temperature of 55 to 60°C., for a period of 25 minutes.</p> <p>A Udylite bath contains a solution commercially available from the America company Udylite for bright nickel plating. The solution is an aqueous solution containing 300 g of nickel sulphate, 50 g of nickel chloride and 40 g of boric acid per litre. The pH is in the range of from 2.8 to 4.5.</p> <p>Decorative chromium-plating in a conventional bath containing chromic and sulphuric acids for a period of 2 minutes at 25 A/dm<sup>2</sup> and at 50 to 55°C.,</p> <p>Rinsing and drying in air.</p> <p>Under these conditions, it is readily possible to obtain reproducibly a highly adherent decorative chromium finish which withstands without blistering heating for one hour to 250°C., followed by cooling in cold water; and does not show any signs of corrosion after exposure for 200 hours to a saline spray normalised with sodium chloride at 35°C.</p>								
35	<p><b>EXAMPLE 2</b></p> <p>The following procedure is adopted for electrolytically coating bars extruded from Al 99.5:</p> <p>Degreasing and pickling in a bath containing 50 g/litre of soda for a period of 5 minutes at 50°C.,</p>								
40	<p>Rinsing, Preparation of the cathodic surface in the following bath:</p> <table><tr><td>Zinc (in fluoborate form)</td><td>20 g/litre</td></tr><tr><td>Nickel (in fluoborate form)</td><td>16 g/litre</td></tr><tr><td>pH value</td><td>3.8</td></tr></table>			Zinc (in fluoborate form)	20 g/litre	Nickel (in fluoborate form)	16 g/litre	pH value	3.8
Zinc (in fluoborate form)	20 g/litre								
Nickel (in fluoborate form)	16 g/litre								
pH value	3.8								
45	<p>Current density 1 A/dm<sup>2</sup>, i.e. a voltage across the terminals of 3 volts,</p> <p>Duration: 45 seconds, Temperature: 30°C., Anodes: stainless steel 18/8,</p>								

- Rinsing,  
Alkaline copper plating in the following bath:
- 5      Cuprous cyanide      26 g/litre  
        Potassium cyanide      46 g/litre  
        Sodium carbonate      30 g/litre  
        Rochelle salt      32 g/litre  
        pH value      11.6
- 10      for 4 minutes at 1 A/dm<sup>2</sup> and at 45°C.,  
        giving a coating around 1 micron thick,
- Rinsing,  
Electrolytically coating in the following bath:
- 15      Tin (in the form of sodium  
        stannate)      40 g/litre  
        Free soda      9 g/litre  
        Crystalline sodium acetate      15 g/litre
- 20      Temperature: 75°C.,  
        Current density: 1.5 A/dm<sup>2</sup>, i.e. a voltage  
        across the terminals of 2.5 volts,  
        Duration: 50 minutes,  
        Thickness of coating: 15 microns,  
        Rinsing and drying in air.
- 25      Under these conditions, it is readily possible reproducibly to obtain a highly adherent coating which withstands without blistering 1 hour's heating to 250°C., followed by cooling in cold water; and does not show any signs of corrosion after exposure for 200 hours to a saline spray normalised with sodium chloride to 35°C.
- 30      **EXAMPLE 3**  
        The following procedure is adopted for the cadmium-plating of components rolled from A-U4G:
- 35      Chemical degreasing in the following bath:
- Trisodium phosphate      10 g/litre  
        Sodium carbonate      10 g/litre
- for a period of 2 minutes at 80°C.,
- 40      Rinsing,  
        Pickling in the following bath:
- Nitric acid 40° Be      300 cc.  
        Water      700 cc.,  
        Sodium fluoride      10 g.
- 45      for a period of 5 minutes at 25°C.,
- 50      Rinsing,  
        Preparing the cathodic surface in the following bath:
- Zinc (in fluoborate form)      20 g/litre  
        Nickel (in fluoborate form)      16 g/litre  
        pH value      3.6
- Current density 1 A/dm<sup>2</sup>, i.e. a voltage across the terminals of 3 volts,  
Duration: 45 seconds,  
Temperature: 30°C.,  
Anodes: graphite,
- 55      Rinsing,  
        Alkaline copper plating in the following bath:
- Cuprous cyanide      26 g/litre  
        Potassium cyanide      46 g/litre  
        Sodium carbonate      30 g/litre  
        Rochelle salt      32 g/litre  
        pH      11.6
- 60      for a period of 4 minutes at 1 A/dm<sup>2</sup> and 45°C., giving a coating around 1 micron thick,
- 65      Rinsing,  
        Cadmium plating in the bath:
- Cadmium cyanide      60 g/litre  
        Sodium cyanide      120 g/litre  
        pH      12.2
- 70      for a period of 25 minutes at 1 A/dm<sup>2</sup> and at 20 to 25°C., giving a coating around 12 microns thick,
- 75      Rinsing,  
        Chromium plating by 5 minutes' immersion at room temperature in the following bath:
- Sodium bichromate      80 g/litre  
        Sulphuric acid 66° Be      8 g/litre  
        Sodium chloride      1 g/litre
- 80      Under these conditions, it is readily possible reproducibly to obtain a high adherent coating which withstands without blistering 1 hour's heating to 250°C., followed by cooling in cold water; and does not show any signs of corrosion after 200 hours' exposure to a saline spray normalised with sodium chloride at 35°C.
- 85      **EXAMPLE 4**  
        The following procedure is adopted for silver-plating components rolled from A-G3:
- 90      Chemical degreasing in the following bath:
- Trisodium phosphate      10 g/litre  
        Sodium carbonate      10 g/litre  
        for a period of 2 minutes at 80°C.,
- 95      Rinsing,  
        Degreasing in a sulphochromic mixture for a period of 5 minutes at 55 to 60°C.,
- 100

- 4
- Rinsing,  
Preparing the cathode surface in the following bath:
- 5      Zinc (in fluoborate form)      16 g/litre  
       Nickel (in fluoborate form)      13 g/litre  
       pH value      4.0
- Current density: 1 A/dm<sup>2</sup>, i.e. a voltage across the terminals of 3 volts,  
Duration: 45 seconds,  
10      Temperature: 30°C.,  
       Anodes: graphite,
- Rinsing,  
Pre-silver plating in the following bath:
- 15      Silver cyanide      5 g/litre  
       Sodium cyanide      60 g/litre
- for a period of 15 seconds at 2 A/dm<sup>2</sup> and at 25 to 28°C.,
- No rinsing,  
Thick silver-plating in the following bath:
- 20      Silver cyanide      30 g/litre  
       Potassium cyanide      55 g/litre  
       Potassium carbonate      45 g/litre
- for a period of 90 minutes at 0.5 A/dm<sup>2</sup> and at 25 to 28°C., giving a coating 25  
25      microns thick,
- Rinsing, and  
Drying in air.
- 30      Under these conditions, the silver coating thus obtained is highly adherent, withstands without blistering 1 hour's heating to 250°C., followed by cooling in water, and shows hardly any signs of corrosion after 200 hours' exposure to a saline spray normalised with sodium chloride at 35°C.
- 35      **WHAT WE CLAIM IS:—**  
1. A process for preparing the surface of
- aluminium or its alloys before metal coating by electrolytic deposition, comprising, after pickling, subjecting the components immersed in an acid bath of zinc and nickel fluoborates and connected to the negative pole of a generator, to the action of a current for a period of from 5 seconds to 300 seconds.  
2. A process as claimed in claim 1 wherein the components are subjected to the action of a current for a period of from 20 seconds to 60 seconds.  
3. A process as claimed in claim 1 or 2, wherein the concentration of fluoborates in the bath amounts to from 5 g to 100 g per litre of each of the metals zinc, and nickel, the pH value being in the range of from 2 to 6.  
4. A process as claimed in claim 3, wherein the concentrations of fluoborates in the bath amounts to from 10 to 30 g per litre of each of the metals zinc and nickel.  
5. A process as claimed in claim 3 or 4, wherein the pH value is in the range of from 3.5 to 4.5.  
6. A process as claimed in claim 2, wherein the temperature of the bath is in the range of from 10 to 80°C., the current density used being in the range of from 0.1 to 10 A/dm<sup>2</sup>.  
7. A process as claimed in claim 6, wherein the temperature of the bath is in the range of from 20 to 35°C, the current density used being in the range of from 0.5 to 2 A/dm<sup>2</sup>.  
8. A process as claimed in claim 1 substantially as herein described with reference to any of the specific examples.  
9. An aluminium alloy when treated by a process as claimed in any of claims 1 to 8.  
10. An aluminium alloy as claimed in claim 9, coated with copper, nickel, chromium, tin, silver or cadmium.
- 40  
45  
50  
55  
60  
65  
70  
75
- ELKINGTON & FIFE,  
Chartered Patent Agents,  
High Holborn House,  
52/54 High Holborn,  
London WC1V 6SH.  
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1972.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.